

Copyright
by
Neha Anand
2018

**The Report Committee for Neha Anand
Certifies that this is the approved version of the following Report:**

Review of Asphaltene Properties and Precipitation Modeling

**APPROVED BY
SUPERVISING COMMITTEE:**

Quoc P. Nguyen, Supervisor

Zoya Heidari

Review of Asphaltene Properties and Precipitation Modeling

by

Neha Anand

Report

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Master of Science in Engineering

The University of Texas at Austin

December 2018

Acknowledgements

I would like to express my sincere gratitude and appreciation to Dr. Quoc P. Nguyen for his guidance and encouragement on this research project and throughout my time at the University of Texas at Austin. I would also like to extend my thanks to Dr. Zoya Heidari for her time to read and review my work. Finally, I would like to express my deep gratitude to my loving parents and siblings, my boyfriend and his amazing family, my supportive friends and my diligent research colleagues without whom this journey would not have been possible.

Abstract

Review of Asphaltene Properties and Precipitation Modeling

Neha Anand, MSE

The University of Texas at Austin, 2018

Supervisor: Quoc P. Nguyen

Asphaltenes are of special interest to the petroleum industry due to their complex, non-linear phase behavior and tendency to deposit in reservoir and production equipment that drives up production and remedial costs associated with oil recovery processes. Precipitated asphaltenes impart high viscosity to residual oil, plug pore throats, alter wettability and reduce hydrocarbon mobility. They are hard to characterize and pose problems even at higher temperatures and for light oils. Thus, the ability to predict transport and thermodynamic behavior of asphaltenic systems is crucial to ensure economic recovery of oil and reduce flow assurance issues. This work summarizes a detailed literature review of the current state of asphaltene science covering critical asphaltene properties such as molecular structure, chemical composition, asphaltene-crude oil phase behavior, transport properties and solubility parameters. The various theoretical approaches such as thermodynamic, scaling and artificial intelligence-based models to predict asphaltene precipitation have been described in detail and compared. This critical review encapsulates merits and demerits of the most prominent approaches

and identifies further scope for improvement. The findings of this work are expected to form the basis of building a fully compositional simulator to predict asphaltene precipitation, flocculation and deposition that is in agreement with the experimentally obtained asphaltene properties.

Table of Contents

List of Tables	viii
List of Figures	ix
Chapter 1: Introduction	1
Chapter 2: Asphaltene Properties.....	4
Chapter 3: Asphaltene Precipitation Modeling.....	11
Thermodynamic Models	15
Solubility Models.....	15
Solid Models	17
Equation of State Models.....	19
Cubic Equation of State	20
Cubic Equation of State plus Association (CPA)	22
Statistical Equation of State	24
Thermodynamic Micellization Models.....	27
Chapter 4: Conclusions and Future Work.....	28
Appendix A	32
Critical Property Correlations.....	32
Peng-Robinson EoS	32
Gamma distribution function	33
Cubic plus Association (CPA) EoS	34
Perturbed Chain Statistical Fluid Association Theory (PC-SAFT) EoS	36
Nomenclature.....	38
References.....	40

List of Tables

Table 1. PC-SAFT parameter correlations for saturates.	37
Table 2. PC-SAFT parameter correlations for aromatics + resins.	37

List of Figures

Figure 1. Simplified petroleum fractionation method (Speight 2004).....	1
Figure 2. Yen-Mullins model (Mullins et al. 2012).....	5
Figure 3. Asphaltene Colloidal Model (Priyanto et al. 2001).....	8
Figure 4. P-T asphaltene deposition envelope.	12
Figure 5. De Boer Plot (De Boer et al. 1995).	13
Figure 6. Three-phase vapor/liquid/solid flash algorithm by Nghiem et al. (1993).	19
Figure 7. CPA modeling approach (Li and Firoozabadi 2010).	23
Figure 8. PC-SAFT Helmholtz Energy Calculations (Ting et al. 2003).....	25
Figure 9. PC-SAFT methodology.	25

Chapter 1: Introduction

Asphaltene constituents are polydisperse, high-molecular weight and the most polar constituents in the crude oil. Asphaltenes are operationally defined on the basis of the solution properties of the petroleum residuum in various solvents and is shown schematically in Figure 1. Asphaltenes are complex molecules that are described as the fraction that is soluble in aromatic solvents such as benzene and toluene but insoluble in low molecular weight n-alkanes such as heptane and pentane (James G. Speight, Long, and Trowbridge 1984). The amount and characteristics of asphaltenes in petroleum varies with source, depth of burial, API gravity of the crude oil, the sulfur content as well as the non-asphaltene sulfur (Koots and Speight 1975).

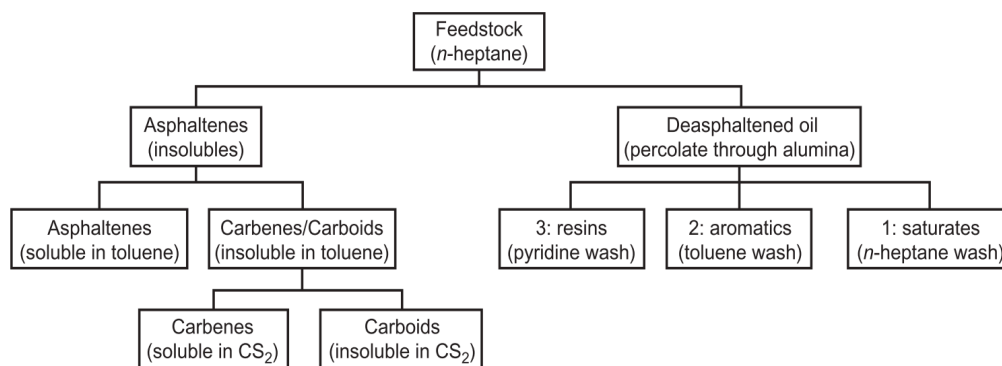


Figure 1. Simplified petroleum fractionation method (J G Speight 2004).

The precipitation of asphaltenes in the reservoir is caused by a wide variety of factors such as changes in pressure, temperature, chemical composition of the crude oil, injecting/mixing diluents or other solvents, electro-kinetic effects and acid stimulation (Koots and Speight 1975). The major factors affecting the deposition of asphaltene inside the reservoir are:

- 1. Compositional changes in reservoir fluids:** During primary recovery, the oil experiences a decrease in gas-oil ratio (GOR) and an increase in the density of the fluids. Both these effects typically reduce the asphaltene flocculation tendency of the reservoir fluid because both gas and asphaltenes compete for solvency in the crude oil so when the light ends decrease in concentration in the oil, asphaltenes can increasingly dissolve into the solution. Consequently, as production time increases, the pressure decreases, the oil becomes heavier and asphaltene issues decrease.
- 2. Injection of Fluids:** Enhanced oil recovery processes involving miscible and immiscible flooding of crude oil reservoirs by light hydrocarbon gases, carbon dioxide and other injection gases significantly alter the flow and phase behavior of the reservoir fluids and rock properties. Asphaltene issues increase as diluent concentration increases in the oil.
- 3. Electro-Kinetic Effects:** Large draw-downs that result in higher fluid velocities in the formation and wells aid in asphaltene flocculation near the wellbore by electro-deposition. To reduce deposition by kinetic effects, the velocity of the fluids in the reservoir should be kept small during initial production, excessive choking should be avoided, and for asphaltenic oils, the wells should be thoroughly cleaned after shut-ins or workovers.

The precipitated asphaltenes reduce the near wellbore reservoir permeability by causing formation damage and plug-up the well-bores and well tubings. Deposition of asphaltenic scales causes operational problems and safety hazards and decreases production efficiency, thereby driving up remedial and operational costs. Therefore,

study of asphaltenes, their properties and predicting the extent of asphaltene precipitation, flocculation and deposition is of considerable interest to the petroleum industry.

Mechanical and chemical cleaning or reservoir condition manipulation are currently utilized solutions to manage asphaltene issues. To better control asphaltene precipitating conditions, practices such as continuous monitoring of well parameters, operating the flowing well head at a higher temperature, decreasing the dissolved gas-oil ratio, reducing the pressure to just below the bubble point pressure and utilizing insulating annular fluids to decrease heat losses should be employed. Furthermore, the asphaltene deposition process can be controlled to a certain degree by injecting additives with peptizing agents into the reservoir. Finally, building accurate asphaltene models that are capable of predicting asphaltene behavior in different scenarios should help in reducing asphaltene problems.

In order to build and verify the results of the asphaltene model, it is important to do a thorough literature review of the relevant asphaltene properties to be utilized for modeling. This report summarizes the relevant asphaltene properties covered in literature, how they are relevant for the asphaltene precipitation modeling process and how these properties are obtained either experimentally or theoretically.

Chapter 2: Asphaltene Properties

In contrast to wax and gas hydrates, modeling asphaltene phase behavior is especially difficult because they are not well characterized. Aspects like higher asphaltene deposition for light oils (low in asphaltene content and viscosity) than heavy oils (high in asphaltene content and viscosity), or the ability of asphaltenes to deposit even at higher temperatures makes the problem even more complicated (Panuganti et al. 2013). Therefore, it is highly important to measure chemical, physical and transport properties of asphaltenes to better understand and predict their phase behavior using analytical and simulation tools. Accurate knowledge of these properties will be critical in evaluating the results obtained from phase behavior predictive tools as well. For this reason, this chapter summarizes important asphaltene properties. Chapter 3 will provide information on how these properties are utilized in asphaltene precipitation models.

The major asphaltene properties covered in literature are as follows:

Molecular Structure: Asphaltene molecules are polydisperse in nature (i.e. particles of variable sizes) and hence, don't possess a precise chemical identity or formula. Recent advancements in the asphaltene science has delivered promising models such as the Yen-Mullins model proposed by Mullins et al. (2012) that elucidates some of the observed phenomena for asphaltenes. They hypothesize that asphaltenes have an "island" molecular architecture that consists of one dominant aromatic ring system with peripheral alkanes (as shown in Figure 2). At small concentrations, these molecules form nano-aggregates with aggregation numbers of approximately 6 and at higher concentrations, these aggregates form clusters with aggregation numbers of approximately 8.

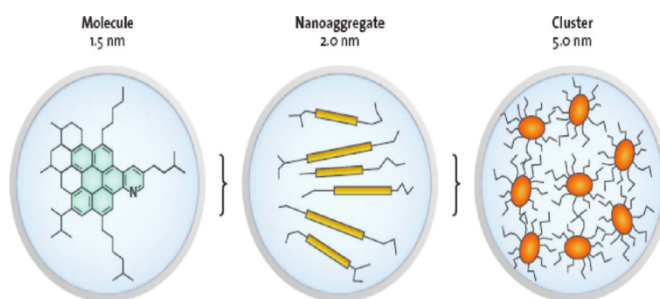


Figure 2. Yen-Mullins model (Mullins et al. 2012).

Chemical Composition: Asphaltenes are typically dark brown to black friable solids that have no fixed melting point and decompose to form a carbonaceous residue when heated. They are elementally composed of hydrogen (H), nitrogen (N), oxygen (O) and sulfur (S), and trace amounts of iron, vanadium and nickel. The carbon number is in the range of 40–80 while the carbon to hydrogen ratio (C/H) is 1:1.2 depending on the source of the asphaltenes (Sheu 2013). It has been reported that the lower H/C ratios and higher N/C, O/C and S/C ratios are observed with n-heptane asphaltenes as compared to n-pentane asphaltenes. This indicates a higher degree of aromaticity and a higher proportion of heteroelements in n-heptane asphaltenes as opposed to n-pentane asphaltenes (Koots and Speight 1975).

Molecular Weight: Several molecular weight ranges have been reported in literature since the asphaltenes were derived using different solvents and concentrations and utilized vastly different measurement techniques. Some common techniques used to estimate the molecular weight of asphaltene are vapor-pressure osmometry, viscometry, boiling point elevation, freezing point depression, light scattering, gel permeation chromatography, fluorescence depolarization, ultracentrifuge, electron microscope studies (Panuganti et al. 2013). Although, mass spectrometry (MS) and molecular diffusion are

the two primary methods that have used to obtain asphaltene molecular weight most frequently.

Results published using a wide variety of measurements have converged to the conclusion that asphaltene molecular weights follow a monomodal distribution with the most probable molecular weight around 750 Da (+/-200) and a range between 500–1000 Da (Mullins et al. 2008). There is significant scope for further research to understand variation in molecular weight of asphaltenes obtained from different sources such as coal, bitumen, petroleum etc. Additionally, it is pertinent to understand variation in measurements obtained using different techniques and to accurately quantify errors rates associated with each technique.

Density: The density of petroleum derived asphaltene at ambient conditions lies between 1 and 1.3 g/cm³ based on the origin and methodology. Some common measurement techniques include isothermal, isobaric ensemble dynamic molecular simulations followed by energy minimization and helium displacement (Yarranton and Masliyah 1996; Rogel and Carbognani 2003).

Viscosity: Increased asphaltene content and low temperature significantly increase the oil viscosity (Sirota and Lin 2007). Presence of precipitated asphaltene particles results in a remarkable increase in oil viscosity at and after the onset of flocculation, hence can useful to detect the onset of asphaltene precipitation (Escobedo and Mansoori 1997).

Mass Diffusion Coefficient: Asphaltene diffusion coefficient is a function of concentration which determines the size of the asphaltene aggregates. At low concentration, aggregation numbers are low, but as the concentration increases, aggregation numbers increase. This implies that higher the concentration, higher will be the state of association resulting in a larger entity size and thereby, lower diffusion

coefficient. The diffusion coefficient of asphaltene in toluene is in the order of 10^{-10} m²/s for a particle size of 1–2 nm or at infinite asphaltene dilution (J-A Östlund et al. 2002; Jenny-Ann Östlund, Andersson, and Nydén 2001).

Solubility Parameter: If asphaltene is considered as a soluble species, solubility parameter can be used to explain asphaltene phase behavior. The Hildebrand solubility parameter for a non-polar, non-hydrogen bonding fluid is given as

$$\delta = \sqrt{CED} = \sqrt{\frac{\Delta H - RT}{V_m}},$$

where CED is the cohesive energy density, ΔH is the energy of vaporization, V_m is the molar volume of the liquid, R is the gas constant, and T is the temperature. CED reflects the degree of van der Waals forces holding the molecules together. The solubility of two materials is only possible if they have similar intermolecular attractive forces i.e. they have similar solubility parameters (Burke 1984). Asphaltenes have the highest solubility parameter among all crude oil components which is estimated to be between 19 and 24 MPa^{0.5} (Wang and Buckley 2001).

When high concentrations of low molecular weight hydrocarbons are dissolved into the liquid phase, the solubility parameter of oil reduces, thereby triggering asphaltene precipitation. Similar changes are expected when temperature or pressure conditions are varied significantly.

Rate of Precipitation: Asphaltene precipitation can be described as the growth of primary particles from a solution due to super-saturation until the system reaches an equilibrium asphaltene concentration. There is scarcity of data available on the rate of asphaltene precipitation. Khoshandam and Alamdari (2010) reported spectrophotometry data on 0.1 g of asphaltene/L of toluene mixed with a 50 volume % n-heptane solution,

which was approximately modeled using a first-order precipitation rate constant of 0.01 min^{-1} .

Aggregation is defined as the agglomeration of primary particles forming larger, secondary particles (asphaltene aggregates) at higher concentrations of asphaltenes in the solution. Most of the available literature currently doesn't differentiate between precipitation and aggregation due to the difficulty in detecting the onset of asphaltene precipitation through microscopes of limited resolution power.

Asphaltene-crude oil phase behavior models: Asphaltene-crude oil behavior is modeled mainly based on two different thermodynamic models: colloidal and solubility models.

The colloidal approach assumes that asphaltenes are suspended in the oil as solid particles. The stability of asphaltene is explained in terms of a micelle formation where asphaltenes self-associate into aggregate structures to form the core onto which the resins adsorb (as shown in Figure 3).

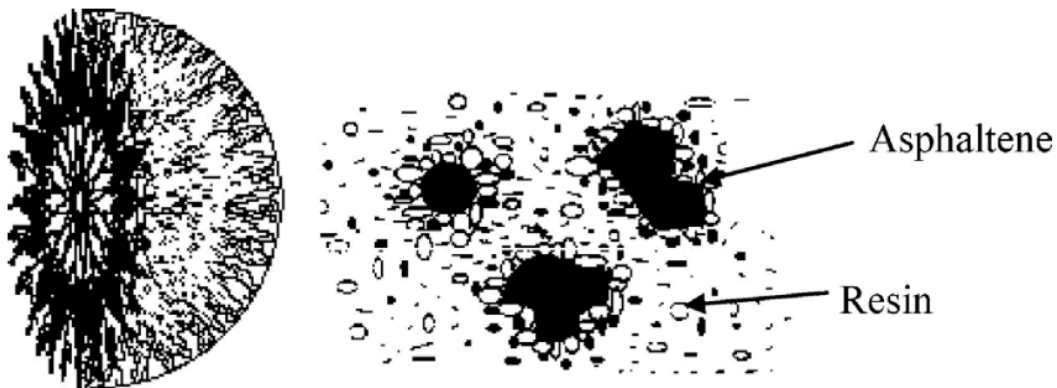


Figure 3. Asphaltene Colloidal Model (Priyanto, Mansoori, and Suwono 2001).

The solubility models assume that the asphaltenes are dissolved in the oil, thereby, forming a homogenous liquid solution. The asphaltene precipitation process can be modeled either as solid-liquid or liquid-liquid equilibrium and is considered reversible.

Chapter 3 discusses in detail various models using these two approaches and sheds some light on some other newer techniques to model asphaltene-oil phase behavior.

Asphaltene Extraction using different Paraffinic Solvents: Asphaltene constituents are insoluble in n-pentane (or in n-heptane) while resins are soluble in n-pentane (or in n-heptane), but insoluble in liquid propane (Koots and Speight, 1975; Andersen and Speight, 2001). The remaining portion of the oil is comprised of saturates and aromatics.

Asphaltenes are obtained from petroleum by adding a nonpolar solvent with a surface tension lower than that of 25 dyne cm^{-1} at 25°C (77°F). Suitable liquids used for this purpose are low-boiling petroleum naphtha, petroleum ether, n-pentane, iso-pentane, n-heptane etc. This is because asphaltene constituents are soluble in liquids with a surface tension above 25 dyne cm^{-1} , such as pyridine, toluene, and benzene.

The separation procedure followed for extraction of asphaltenes and resins not only dictates the yield but also the quality of the fraction. For example, the use of different paraffinic solvents for extraction can influence the yield by a considerable factor. The technique employed also dictates whether or not the resins co-precipitate with asphaltenes or not (J G Speight 2004). The difference in the yield of the asphaltene fraction is related to the variation in the solubility parameter of the hydrocarbon solvent (Mitchell and Speight 1973).

As the carbon number of the solvent decreases, the extent of asphaltene flocculation and particle size increases (Arya et al. 2016). For example, propane and butane cause much more severe asphaltene precipitation as compared to n-heptane, which

results in lesser viscosity reduction in the case of n-heptane (Arciniegas and Babadagli 2014). This also implies that the Hildebrand solubility parameter decreases with decrease in carbon number since asphaltene miscibility is higher with lower carbon number solvents.

The n-heptane asphaltenes differ substantially from the n-pentane asphaltenes especially when comparing the elemental composition. The hydrogen-to-carbon atomic ratio of the n-heptane precipitate is lower while nitrogen-to-carbon, oxygen-to-carbon, and sulfur-to-carbon ratios are usually higher than that of the n-pentane precipitate. This indicates a higher degree of aromaticity and higher proportions of the hetero elements in the n-heptane precipitate (Andersen and Speight 1999).

Asphaltene properties also vary with separation method and individual measurement technique. Some other critical factors other than solvent type are contact time, solvent-to-crude oil ratio and temperature.

Chapter 3: Asphaltene Precipitation Modeling

Asphaltene precipitation can be triggered by changes in pressure, temperature, and addition of light hydrocarbon components. Several different approaches can be utilized to model asphaltene precipitation in these scenarios; starting with quick screening tools such as the De Boer Plot, which can help identify the asphaltene deposition envelope to full-fledged compositional models that model detailed asphaltene phase behavior to finally artificial intelligence models trained on past data. This chapter has been divided by the modelling approach for asphaltenes. Several researchers have investigated different aspects related to asphaltene precipitation to answer the two main questions: when will precipitation occur and how much asphaltene will precipitate?

Asphaltene precipitation can be visualized using the asphaltene deposition envelope (ADE) in the Pressure-Temperature space as shown in Figure 4. The asphaltene deposition envelope provides upper and lower bounds on the region where precipitation is expected to occur. Precipitation starts to occur above the saturation pressure (Upper ADE pressure) and reaches its maximum at around saturation pressure (liquid to gas transition). It then decreases as pressure drops and finally ceases to exist below the lower ADE pressure. Above saturation pressure (only liquid phase), precipitation takes place solely due to pressure changes, while below the saturation pressure (liquid and gas phases), both composition and pressure affect the precipitation behavior. This makes modeling pressure depletion more difficult since we need to account for variation in both pressure and composition. On the other hand, for solvent injection, if we can keep two variables among pressure, temperature and composition constant and vary the third, we can quantify the impact of a single variable on asphaltene precipitation at a time.

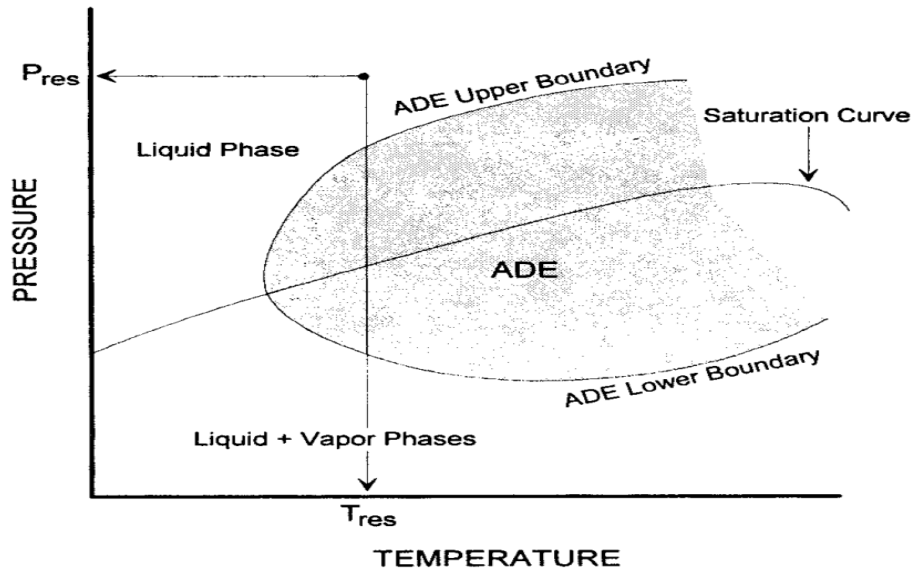


Figure 4. P-T asphaltene deposition envelope.

For primary recovery (i.e. recovery by pressure depletion), the most popular screening method for evaluating risk of asphaltene precipitation during depressurization is the De Boer Plot (as shown in Figure 5). this plot demonstrates the difference between the reservoir pressure and bubble-point pressure with respect to in-situ density of the reservoir fluid. The unstable (severe problems) and stable regions (no problems) are denoted based on calculations of asphaltene supersaturation using the Hirschberg model (Hirschberg et al. 1984). The intermediate region (possible problems) is calculated using supersaturation values between 1 and 2 (assuming the solubility parameter for asphaltene to be $20 \text{ MPa}^{0.5}$). Severe problems are expected with light to medium viscosity oils with low asphaltene content whose initial reservoir pressure is greater than saturation pressure. It is a pessimistic tool since it shows false positives for many field cases, which indicates that asphaltene precipitation would take place where no problems developed in the field (Oilfield Wiki 2016). For this reason, more complicated models have been developed in

the last few decades that describe the asphaltene-crude oil phase behavior more accurately.

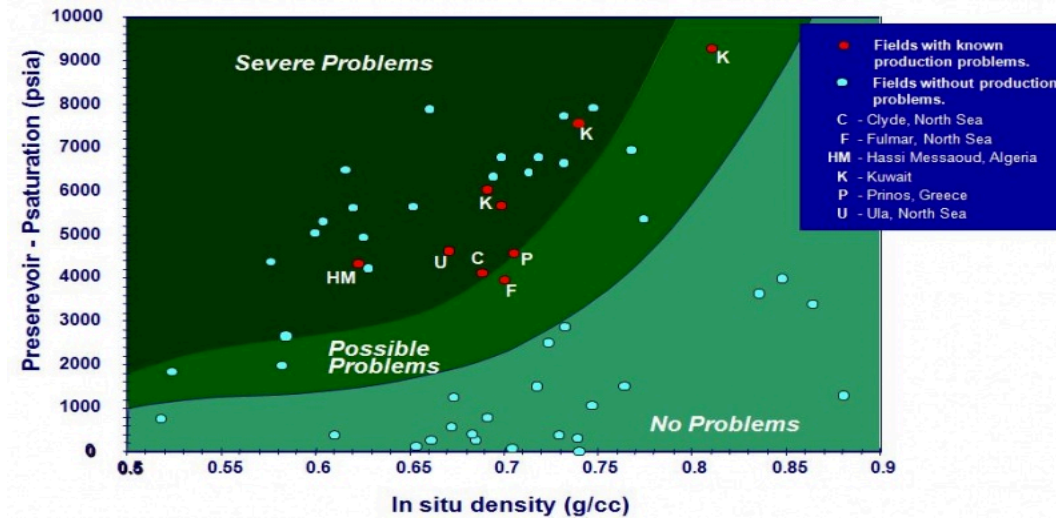


Figure 5. De Boer Plot (De Boer et al. 1995).

According to the vast literature available on this subject, the predictive models for asphaltene precipitation can be classified into three main categories, namely thermodynamic models, fractal aggregation-based models, and connectionist (or intelligence) models. Thermodynamic models are the most widely used techniques to model asphaltene precipitation. Various phase behavior simulators existing in the industry utilize these models.

Two different thermodynamic theories have been proposed to describe the interactions of asphaltene molecules with molecules of other components namely the solubility and the colloidal models. In the first hypothesis, asphaltene molecules are solubilized in oil due to their interactions with other oil molecules. The classical Flory-Huggins model and equation of state-based models are some examples in this category. In the less commonly used second theory, it is hypothesized that colloids form due to

attractive polar forces between asphaltene and resin molecules. The stability of these colloids in the oil is dependent upon the pressure, temperature, and composition of the oil. The solid asphaltene colloidal model proposed by Leontaritis and Mansoori (1987) and the thermodynamic micellization model given by Pan and Firoozabadi (2000) are some examples supporting the second hypothesis (Arya et al. 2016). Hence, the thermodynamic models can be further categorized into five subcategories: polymer solubility models, solid models, colloidal models, equation of state and statistical models, and thermodynamic micellization models (Qin et al. 2000; Zendehboudi et al. 2014).

Scaling models form the basis for the aggregation-based methods. These are based on properties of the asphaltene-crude oil mixture such as dilution ratio, GOR, resin to asphaltene ratio, molecular weight of the injected diluent and the residual oil, mole fraction of heavy components, oil specific gravity and other conditions such as pressure and temperature (Bagheri et al. 2009; Hu et al. 2000; Rassamdana et al. 1996).

More recently, artificial intelligence-based models have been proposed to overcome the complexity of existing processes/phenomena. These models utilize Artificial Neural Network (ANN), Bayesian Belief Network (BBN) or other advanced machine learning algorithms to solve for the amount of asphaltene precipitated at given conditions (Javad Sayyad Amin et al. 2010; Zahedi et al. 2009; Zendehboudi et al. 2014). Some of the deterministic tools are limited due to their validity at specific process conditions and their reliance on linear system identification models, whereas the asphaltene precipitation/deposition phenomenon is strongly non-linear in terms of process and thermodynamic parameters. ANN techniques are strong candidates to model this kind of non-linear relationship between the input variables and the target parameter. Additionally, smart and proficient techniques such as ANN can also estimate any discontinuous function that relates the output to the input vectors. As compared to

conventional methods, connectionist modeling methods save considerable time and resources.

Despite the popularity of thermodynamic and scaling models, both of these approaches present considerable drawbacks in predicting asphaltene precipitation. They need extensive data points or do not work well within a wide range of pressure, especially at high pressure conditions. It has been reported that more acceptable quantitative and qualitative agreement between experimental data and predicted amount of asphaltene precipitation and higher accuracy was obtained using ANN model as compared to scaling equations (Ashoori et al. 2010). However, techniques utilizing artificial intelligence are still relatively new and as such, these methods are not well understood. Their underlying algorithms appear in the form of black boxes, which decreases the interpretability of results and makes it more difficult to derive specific relationships between the target parameter(s) and control variables. Additionally, most of the intelligent models require a relatively large volume of data and they are not applicable in the absence of adequate real datasets (J. Sayyad Amin, Alimohammadi, and Zendehboudi 2017).

The following sections discuss the various thermodynamic models in more detail. Thermodynamic models are the primary focus of this literature review since they remain the most widely used models utilized for modeling asphaltene precipitation. The most prominent thermodynamic models have been compared and their inputs and methodologies have also been specified.

THERMODYNAMIC MODELS

Solubility Models

The solubility models are based on the simplified version of the classical Flory-Huggins theory (Flory 1942). Hirschberg model (Hirschberg et al. 1984), Cimino model

(Cimino et al. 1995) and Nor-Azlan model (Nor-Azlan and Adewumi 1993) are some examples of solubility models.

Hirschberg et al. (1984) developed the solubility model to predict the mixing heat of asphaltene/oil which is expressed in terms of the dissimilarity in the solubilities of the asphaltene and the other components in the crude oil. Asphaltene stability is described in terms of reversible liquid-liquid equilibrium and the activity coefficients were calculated using the Flory-Huggins polymer solution theory assuming asphaltene to be a pure component. Their approach also simulates the effects of non-ideality of the resin and asphaltene components on the phase equilibrium calculations. Two pseudocomponents (asphalt (i.e., asphaltenes and resins) and solvent) or three pseudocomponents (asphaltenes, resins and solvent) models were considered, depending upon the conditions, which determine whether the resins are precipitated along with asphaltenes or are separated.

Cimino et al. (1995) proposed a precipitation model utilizing polymer-solution thermodynamics, which leads to a better representation of asphaltene phase behavior. On phase separation, it is assumed that the asphaltene phase nucleates and that it contains both asphaltene components and the solvent. However, it needs extensive experimental data to calculate its parameters, which are highly sensitive to the inconsistencies in the data.

Nor-Azlan and Adewumi (1993) developed another model using statistical thermodynamics of polymer solutions. Material balance combined with the Flory-Huggins theory was applied to predict asphaltene precipitation. First, a Vapor-Liquid (VLE) flash calculation was performed using an Equation of State (EoS) to obtain the vapor and liquid fractions and their compositions. Then, a Liquid-Liquid (LLE) calculation was carried out using the Flory-Huggins theory to obtain the fraction of

asphaltene component by assuming that this doesn't affect the previously VLE calculations. The model is simple and does predict the correct trend but is unable to closely match the experimental precipitation data.

The solubility models are simple to use for asphaltene precipitation, but they are not robust and have poor predictive power. Li and Firoozabadi (2010) state that these models are oversimplified due to the fact that the oil phase contains only two pseudocomponents namely asphaltene and solvent. These models also don't account for association of asphaltene and polar components. In addition, they can't be independently used for live oils below bubble point. For such cases, an EoS will be required first to perform a vapor-liquid split followed by the application of the solubility model on the liquid phase generated to check for asphaltene precipitation. This is based on the assumption that asphaltene precipitation does not affect the vapor-liquid split calculations which might not entirely be valid.

Solid Models

In the solid models, oil and gas phases are modeled using EoS and asphaltene is assumed to be a single component in the solid phase. Asphaltene precipitation is modelled by using a multiphase flash calculation where the fluids phases are described with an equation of state while the fugacity of components in the solid phase are calculated using the solid model. The solid phase can comprise of one or more components.

Nghiem et al. (1993) and Chung (1992) models are two examples of this approach. A crucial step in these models is to characterize the solid-forming components, both in the solution and in the solid phase. The precipitated phase is assumed to an ideal mixture of solid components. The heaviest pseudocomponent in the fluid model is split

into two components, non-precipitating and precipitating fraction. These two fractions may differ in binary interaction and volume shift parameters but have the same critical properties and acentric factors. Using the experimentally calculated value of asphaltene wt.% in the dead oil, the mole fractions of these two pseudocomponents can be calculated. The fluid model with asphaltene component is then tuned to match experimental Pressure-Volume-Temperature (PVT) data. Finally, the amount of solid precipitation can be predicted by using the fugacity equation in solid model. For this purpose, the reference fugacity at the reference pressure and the molar volume of the solid should be known prior to usage. The reference fugacity was set equal to the fugacity of the asphaltene component in the liquid phase. This value can be predicted by the equation of state at a given asphaltene deposition onset pressure. The solid molar volume was set higher than the molar volume of the asphaltene component that is obtained by the EoS calculations. The methodology used by Nghiem et al. (1993) for this three-phase vapor/liquid/solid flash calculation is shown in Figure 6.

The solid models have been widely used in the reservoir simulators and provide acceptable agreement with experimental data, but significant calibration of several tuning parameters is required to generate a robust model for asphaltene phase behavior. Therefore, a major drawback of these thermodynamic models is that they require extensive data points to calculate the EoS coefficients. This is attributed to the complex nature of asphaltenes and uncertainty in estimating the value of asphaltene molecular weight (J. Sayyad Amin, Alimohammadi, and Zendehboudi 2017). Furthermore, these solid models don't take into account asphaltene self-association, which suggests that they ignore the possibility of asphaltene flocculation (Sabbagh et al. 2006).

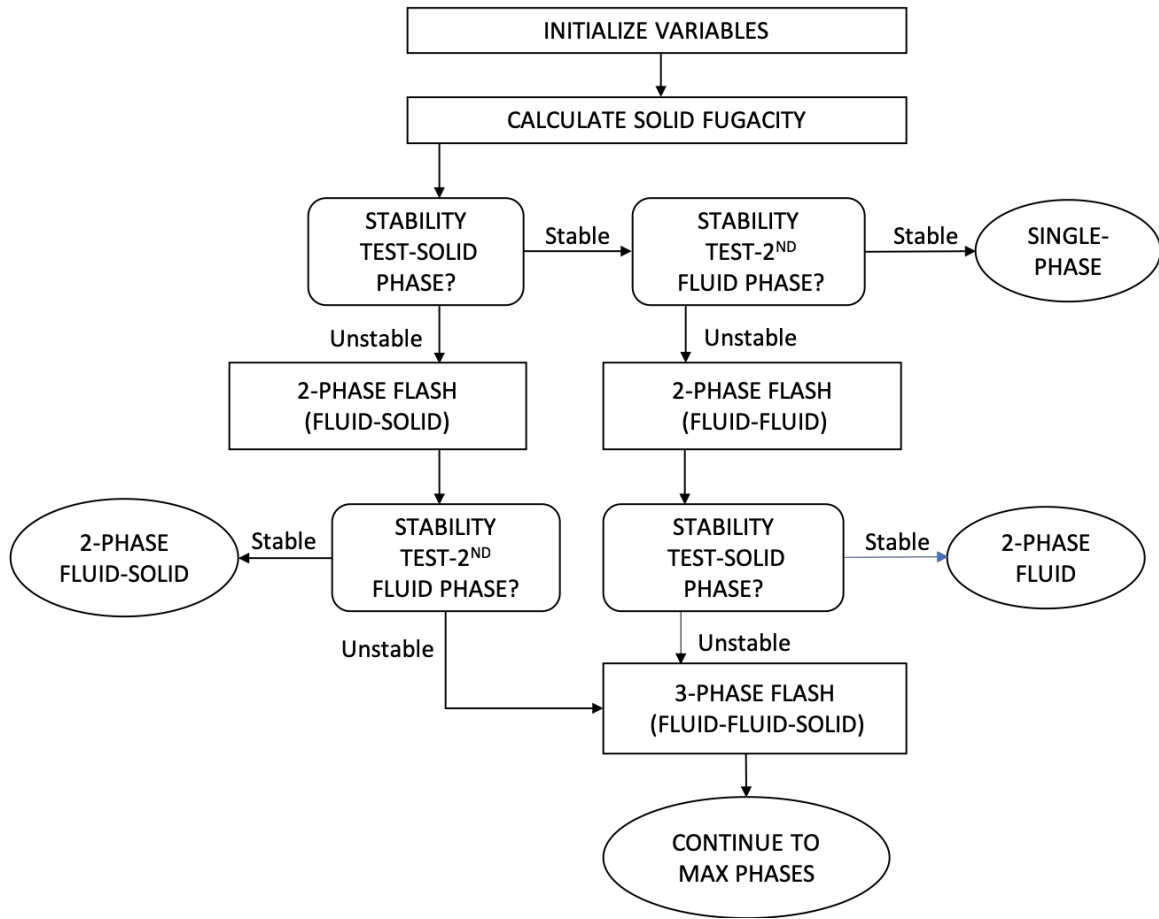


Figure 6. Three-phase vapor/liquid/solid flash algorithm by Nghiem et al. (1993).

Equation of State Models

There are three major equation of state models used for asphaltene modeling:

1. **Cubic Equations of State (CEoS):** Peng-Robinson (PR EoS) and Soave-Redlich-Kwong (SRK EoS) with/without Peneloux volume correction factors lie in this category.
2. **Cubic Equations of State plus Association (CPA):** This category includes Cubic EoS models which account for self-association between asphaltenes and aromatics/resins.

3. Statistical EoS: Statistical EoS are the most recent advancement in the EoS modeling field that have been developed to deal with asymmetric mixtures. SAFT (Statistical Associating Fluid Theory) and PC-SAFT (Perturbed Chain SAFT) belong to this category.

The detailed methodology for implementing these EoS models is described in the following subsections. The relevant mathematical equations for these models are shown in Appendix A.

Cubic Equation of State

Cubic EoS represent the industry standard for simulating the phase behavior of reservoir fluids; especially the Soave-Redlich-Kwong (SRK) and the Peng-Robinson (PR) equations are the most commonly used models. These models are commonly applied with a volume correction/translation factor to better match molar liquid volumes and densities. With the inclusion of the volume correction factor, these models are capable of predicting the phase behavior of reservoir fluids in terms of saturation points and gas-liquid ratios.

The most popular cubic EoS used for asphaltene modeling is the Peng-Robinson EoS, which is especially suited for light oils. The required inputs include the SARA analysis (Saturate, Aromatics, Resin and Asphaltene), molecular weights, and densities of SARA fractions, fractional asphaltene precipitation in solvents and asphaltene yields from alkane-diluted heavy oils or bitumen. A general methodology utilizing PR EoS and these inputs is discussed next.

The oil can be characterized in two ways: Using detailed NBP cuts which are fitted by a distribution function such as Gaussian distribution or by using SARA (Díaz et al. 2011; Sabbagh et al. 2006). The latter approach involves dividing bitumen into two

fractions: Saturates + Aromatics + Resins (S+A+R) and asphaltenes. Critical properties of these fractions are determined by using appropriate critical property correlations (as shown in Appendix A). Liquid-liquid equilibrium is assumed between a heavier liquid phase and a lighter liquid phase but only asphaltene is allowed to partition between the two phases so that the heavy phase is comprised of only asphaltenes. Asphaltene can be accounted for as a single component or divided into more pseudo-components using molar mass distribution functions such as the Gamma distribution function (as shown in Appendix A). Saturated and aromatic critical properties are determined by fitting asphaltene precipitation data obtained from saturate + toluene and aromatic + heptane solutions respectively. EoS parameters for asphaltenes are varied to fit measured densities, precipitation data for mixtures of asphaltenes, toluene, and heptane. To account for asphaltene self-association, average associated molar mass of the asphaltenes measured at or estimated for the given precipitation conditions can be used.

Despite its popularity, it has been reported that PR EoS modeling is prone to errors in predicting asphaltene precipitation (Díaz et al. 2011; Gao et al. 2016; Gao and Li 2017). A significant failure of the model is its inaccurate prediction of asphaltene precipitation at high dilution. A CEoS when used with conventional mixing rules should ideally predict that asphaltenes become soluble at high dilution ratios but the results show otherwise. This can be avoided by using an unrealistically low molecular weight for the asphaltenes, which gives a relatively larger mole fraction of asphaltenes. However, the underlying issue that lingers is due to the fact that CEoS with conventional mixing laws is not applicable to asphaltenes. Modified mixing rules, asymmetric interaction parameters, and EoS association terms are some suggested solutions.

The CEoS parameters that are tuned to match critical properties, are also not well defined for asphaltene molecules. Panuganti et al. (2012, 2013) showed that a CEoS that

is tuned for particular dataset can fail to predict the asphaltene onset pressure for a different gas injection composition. Additionally, CEoS don't provide accurate results for gas compressibility factors and oil compressibilities (Leekumjorn and Krejbjerg 2013). Another severe limitation of these traditional models is their limited ability to precisely predict the phase behavior of systems (especially liquid density) that comprise of components with vastly different molecular sizes. This is especially true for mixtures of heavy oil and solvents because CEoS models have not been adequately tested for such systems. Their modeling is more challenging because characterization data is not available for the non-distillable (or C30+) fraction of the heavy oil, which can make up more than 50 wt. % of the fluid. Flash calculations are also more complicated because there may be multiple liquid phases at equilibrium. Also, since bitumen behaves as an almost pure non-volatile component, abrupt appearance and disappearance of phases over small pressure or composition changes is observed.

Cubic Equation of State plus Association (CPA)

Cubic EoS can also incorporate an asphaltene self-association term to better account for the associative nature of the asphaltene molecules. Li and Firoozabadi (2010) applied CPA to n-alkane diluted heavy oil and bitumen systems by modeling asphaltene precipitation as liquid-liquid equilibrium. Oil was broken into saturates (S), aromatics + resins (A+R) and asphaltene fractions. It was hypothesized that self-association between asphaltene molecules would result in asphaltene aggregation but cross-association with other polar components such as aromatics and resins may prevent asphaltene aggregation and stabilize asphaltene species. Cross-association factor between asphaltenes and Aromatics + Resins was the only adjustable factor, which depends on temperature, type of alkane and asphaltene, but was independent of Pressure and concentration. Higher the

alkane number, higher the cross-association energy was observed. They investigated the effects of temperature, pressure and compositional changes on asphaltene precipitation. Their approach successfully predicted saturation and onset pressure, amount of precipitated asphaltenes and gas-oil asphaltene three-phase co-existence. Their detailed methodology is shown in Figure 7.

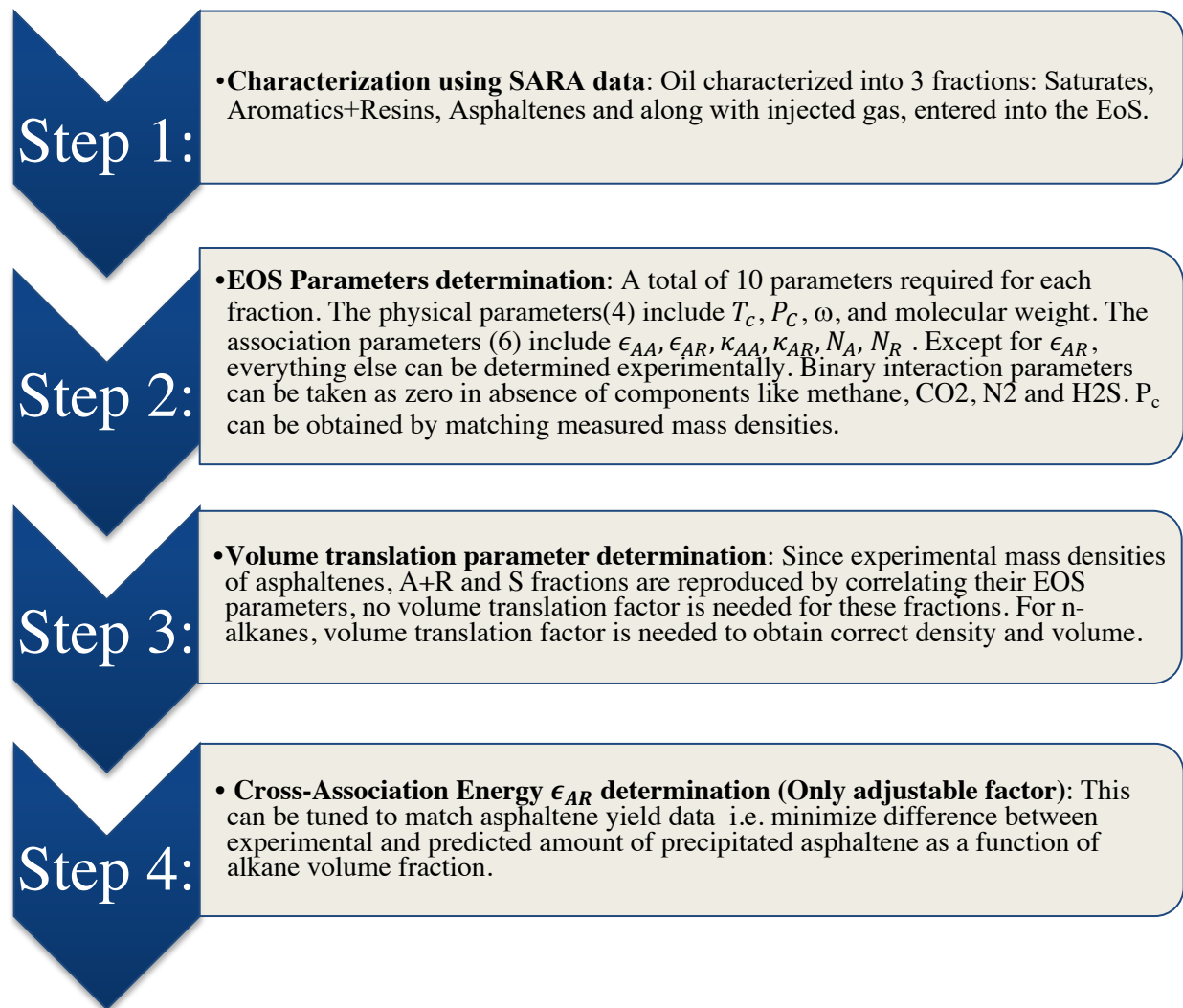


Figure 7. CPA modeling approach (Li and Firoozabadi 2010).

CPA EOS has been applied with limited success in modeling asphaltene behavior, but it requires a lot more parameters than other EoS approaches. Moreover, for a non-associating system, it reduces to the simple CEoS with the same drawbacks as discussed before. For oils with a fairly high concentration of asphaltenes (i.e. approximately 22 wt %), only associating with aromatics/resins may not be sufficient to prevent asphaltene precipitation. Like CEoS, satisfactorily matching experimental asphaltene yield has not been possible even after adjusting association parameters. Finally, onset point of asphaltene precipitation is poorly matched.

Statistical Equation of State

Statistical EoS are one of the most recent developments in the asphaltene science that are deemed to be better equipped to handle asymmetric mixtures. Statistical Associating Fluid (SAFT) theory treats molecules as chains of spherical segments. The fluid's free energy is then determined by the addition of the independent segment free energy and the change in free energy due to chain formation and association (as shown in Figure 8). The perturbed-chain SAFT (PC-SAFT) EoS presented is a modified version of the SAFT EoS, that employs Barker and Henderson's second-order perturbation theory. This theory considers a hard-chain reference that leads to a dispersion term that properly depends on the chain length of a molecule (Gross and Sadowski 2001).

For each non-associating component, three parameters are required in PC-SAFT EoS including Number of segments per molecule (m), temperature independent diameter of each molecular segment (σ) and: segment-segment dispersion (attractive) energy (ϵ). With just three parameters, this EoS is capable of accurately predicting accurate vapor pressures and liquid densities. On the other hand, CEoS with volume translation usually requires four or more parameters to fit the same data. Correlations for these three PC-

SAFT parameters for saturates, aromatics and resin pseudocomponents have been shown Appendix A. The PC-SAFT methodology (Gonzalez et al. 2005; Panuganti et al. 2012, 2013; Zúñiga-Hinojosa et al. 2014) has been shown in detail in Figure 9.

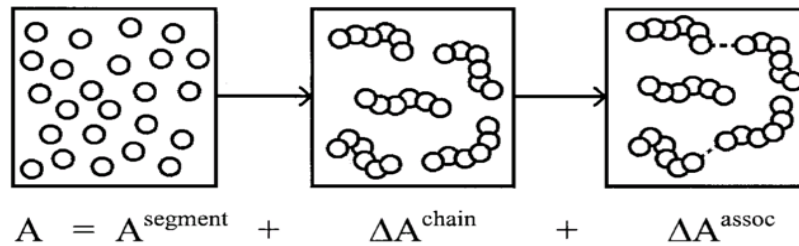


Figure 8. PC-SAFT Helmholtz Energy Calculations (Ting et al. 2003).

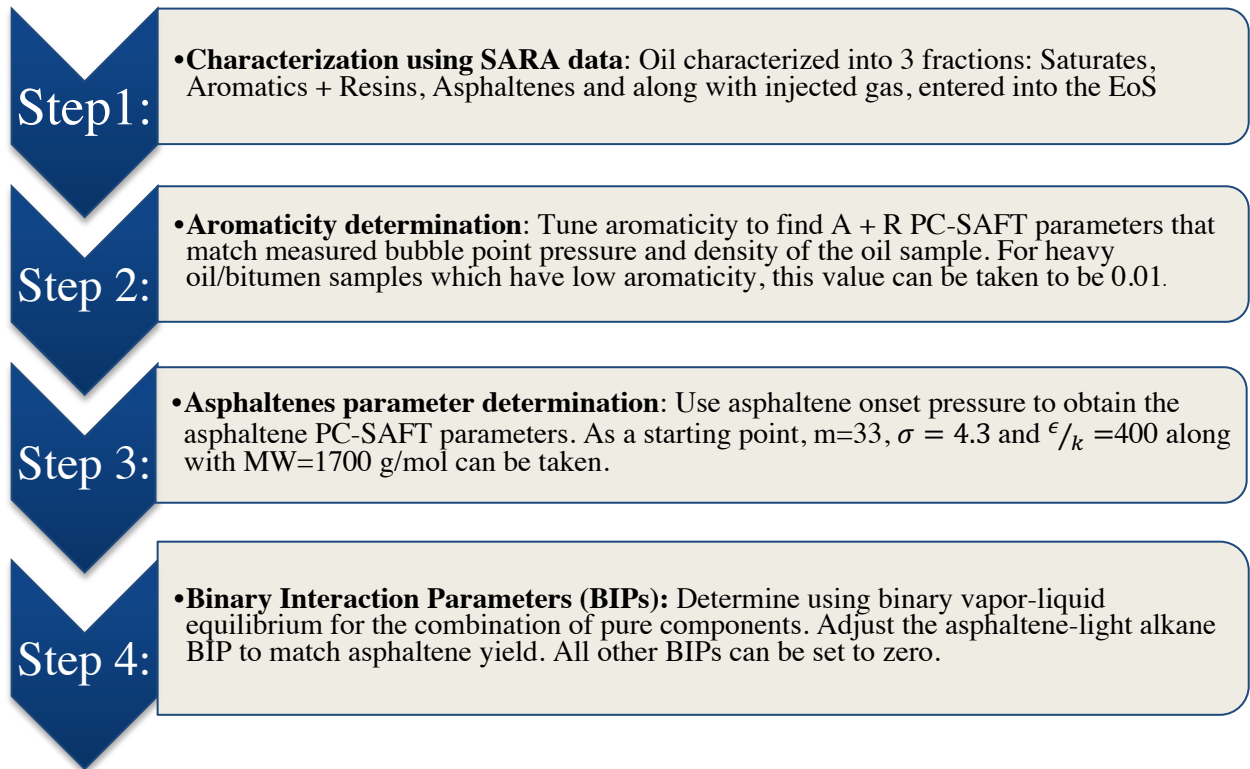


Figure 9. PC-SAFT methodology.

The PC-SAFT equation is superior to the cubic EoS for prediction of gas phase compressibility factors and oil phase compressibilities. It provides accurate results for pressure-dependent phase densities without negatively impacting its ability to simulate saturation points, gas/oil ratio etc. (Leekumjorn and Krejbjerg 2013). These statistical EoS models have also been tested for heavy oil phase behavior; in particular, asphaltene precipitation from live-oils was modeled by Ting and Gonzalez (2007) and Vargas et al. (2009). Majority focus has been on modeling gas solubilities and asphaltene precipitation in heavy oil or bitumen; however, these models have not yet been tested on a broad range of heavy oils and solvent mixtures. Since PC-SAFT is more appropriate for cases when chain length of molecules differ significantly (i.e. between asphaltenes and n-alkanes), it is capable of predicting asphaltene fractional yield and bubble point trends quite accurately for gas injection processes (Gonzalez et al. 2005; Vargas, Gonzalez, Creek, et al. 2009; Vargas, Creek, and Chapman 2010; Zúñiga-Hinojosa et al. 2014).

Unlike the cubic equations, simulating gas injection processes with PC-SAFT can be sometimes problematic since it is not bound to match the pure component critical point. Another major concern is higher computational time for PC-SAFT than CEoS due to higher complexity in finding density roots. Moreover, the PC-SAFT parameter correlations and characterization procedures have not been tested thoroughly as of now.

PC-SAFT and CEoS approaches could also suffer from drawbacks due to usage of SARA (as shown in Figures 7 and 9) for characterizing the oil and solvent system. One disadvantage of the SARA procedure for characterizing the oil sample is that it requires measurement of molar mass which is complicated for heavier hydrocarbons and results may vary depending on the measuring technique. Secondly, variation in SARA results due to the inconsistent measurement techniques is likely as well. Lastly, SARA procedure requires regressing adjustable parameters for each studied oil sample (Saajanlehto and

Alopaeus 2014). Although SARA provides a quick and simple characterization method, in some cases, for better accuracy, more detailed characterization approaches might be more suitable.

Thermodynamic Micellization Models

The micellization model developed by Pan and Firoozabadi (2000) assumes that asphaltene molecules form a micelle core, which is stabilized by the resin molecules that absorb on the surface of this core. The structure and concentration of the micelle is determined by minimizing Gibbs free energy. Although the predicted size of asphaltene micelles in crude oils using this model was in good agreement with the experimental data, the calculated results of the amount of precipitation were not reported. This model is hence, not widely supported by the industry.

Chapter 4: Conclusions and Future Work

This report provides a thorough literature review of critical asphaltene properties and theoretical asphaltene precipitation models. These summary findings can be useful in understanding the current state-of-the-art technologies in the asphaltene science and identifying shortcomings of current methodologies. The key conclusions of this work are noted below.

Asphaltenes are complex, polar, polydisperse and high-molecular-weight components that are operationally defined based on their insolubility in light n-alkanes and solubility in benzene and toluene. Asphaltene precipitation can have serious implications on the cost and complexity of a recovery process based on primary depletion and solvent/gas injection especially for heavy oil applications. Asphaltene deposition can cause pore-throat blockage and alter formation wettability, thereby negatively impacting hydrocarbon mobility. The deposition of these asphaltenic scales can even occur at higher temperatures or for light oils and affect all aspects of oil production, processing and transportation. It is therefore, imperative to accurately identify not only the conditions that allow for asphaltene precipitation but also the amount of asphaltene precipitated.

To build and validate results obtained from these asphaltene precipitation models, properties of asphaltene molecules would be required. The Yen-Mullins model is the most prominent model for explaining the molecular structure of asphaltenes. It is hypothesized that asphaltenes have one dominant aromatic ring system with peripheral alkanes. These molecules form nano-aggregates (approximately 6 aggregation number) at small concentrations and clusters (approximately 8 aggregation number) at higher concentrations. Asphaltenes do not have a distinct chemical composition but contain hydrogen (H), nitrogen (N), oxygen (O) and sulfur (S) with trace amounts of iron,

vanadium and nickel. Their molecular weight lies between 500–1000 Da with an average value of 750 Da. Their density at ambient conditions falls between 1–1.3 g/cm³ and their diffusion coefficient in toluene is in the order of 10⁻¹⁰ m²/s for a particle size of 1–2 nm or at infinite asphaltene dilution. Asphaltene solubility parameter is highest among all crude oil components and lies between 19 and 24 MPa^{1/2}. Asphaltene properties are highly dependent on the solvent and techniques used to extract them. As the carbon number of the solvent decreases, the extent of asphaltene flocculation and particle size increases. Higher degree of aromaticity and higher proportions of the hetero elements are observed in the n-heptane precipitate as compared to n-pentane precipitate.

Over the past few decades, several researchers have attempted to propose theoretical models that predict asphaltene precipitation for primary and enhanced oil recovery applications. A simple and quick tool is the De Boer plot that identifies risk of asphaltene precipitation on a Pressure-Temperature plot. It gives pessimistic results in field applications. Therefore, more complicated models such as thermodynamic models, fractal aggregation-based models, and connectionist (or intelligence) models have been developed. Thermodynamic models are the most widely used models that comprise of polymer solubility, solid, colloidal, equation of state, and statistical and thermodynamic micellization models. Solubility models are deemed to be oversimplified while the solid models do not account for asphaltene flocculation. Cubic EoS models with/without association factors give inaccurate asphaltene yields due to their inherent limitations in modeling longer chain molecules such as asphaltenes. For this reason, statistical EoS models seem more appropriate but are computationally more intensive and less tested on experimental datasets. Thermodynamic micellization models are not suitable for predicting amount of asphaltene precipitated. Fractal aggregation-based models are based on simple scaling equations that utilize properties of the asphaltene-oil-solvent system,

but they are very limited in their application. The latest artificial-intelligence models capture the non-linear asphaltene phase behavior well but require extensive data points to train. In summary, each methodology has certain drawbacks due to the complex nature of asphaltenes but recent methods that account for asphaltene self and cross association such as the CEoS with modified mixing rules and association terms, statistical EoS and artificial-intelligence based models have given promising results and could be improved significantly with more experimental and numerical simulation work. The most important factor to keep in mind would be that the predictions given by these models support the properties of asphaltenes obtained experimentally and do not make oversimplifying or unrealistic assumptions.

The summary of asphaltene properties and details of currently available asphaltene precipitation models were presented in this work with the objective of understanding the current state of research in asphaltene science. These findings lay the foundation for developing an asphaltene-targeted compositional simulator that is capable of predicting asphaltene precipitation, flocculation and deposition. The methodologies presented for each prominent type of precipitation model can be utilized to build a more robust precipitation model for the simulator. A similar literature review would be required to predict how much asphaltene would flocculate and finally deposit onto the surface, so that it is possible to quantify the formation damage caused by asphaltene deposition. This compositional simulator should ideally abide by the physical and chemical characteristics of asphaltenes without making unrealistic assumptions. Moreover, this simulator would be capable of predicting the full phase behavior of asphaltenes (from precipitation to deposition) for a wide variety of use cases such as gas injection, pressure depletion or temperature fluctuation. Lastly, most commercially available simulators for predicting asphaltene phase behavior utilize only thermodynamic

models and do not employ any machine learning techniques. The flexibility to choose between thermodynamic or artificial-intelligence based models can be an added feature of the simulator.

Appendix A

CRITICAL PROPERTY CORRELATIONS

To estimate parameters of cubic equations of state, accurate critical property and acentric factor correlations are required. Most well-known correlations state that these properties of components are functions of molecular weight, specific gravity and normal boiling point. Examples of some commonly used correlations are Lee and Kesler (1975) and Twu (1984).

PENG-ROBINSON EOS

Peng-Robinson EoS, which includes a volume translation factor to better describe liquid densities, was proposed by Robinson and Peng (1978) and is given by

$$P = \frac{RT}{v-b} - \frac{a\alpha(T_r, \omega)}{v(v+b)+b(v-b)},$$

where P is the pressure, T is the absolute temperature, v is the molar volume, R is the universal gas constant, a and b are constants related to attractive and repulsive forces, T_r is the reduced temperature T/T_c , T_c is the critical temperature, ω is the acentric factor and α is a function that helps to tune the EoS and fit it to vapor pressure experimental data. The attractive and repulsive terms for a pure component are a function of its critical temperature T_c and pressure P_c are given by

$$a_i = 0.457235 \frac{R^2 T_{ci}^2}{P_{ci}} [1 + c_i (1 - T_{ri})]^2,$$

$$\text{with } c_i = \begin{cases} 0.37464 + 1.54226 \omega_i - 0.26992 \omega_i^2 & \text{for } \omega_i \leq 0.5 \\ 0.3796 + 1.485 \omega_i - 0.1644 \omega_i^2 + 0.01667 \omega_i^3 & \text{for } \omega_i > 0.5 \end{cases},$$

$$b_i = 0.07777969 \frac{RT_{ci}}{P_{ci}},$$

The tuning parameter α for the PR EoS is a function of the acentric factor and is represented as

$$\alpha(T_r, \omega) = [1 + \omega(1 - T_r^{1/2})]^2.$$

For multicomponent systems, classical mixing rules given by van der Waals (Kwak and Mansoori 1986) can be used to compute a and b terms from the corresponding pure component values, which are given by

$$a = \sum_i \sum_j x_i x_j a_{ij},$$

$$b = \sum_i \sum_j x_i x_j b_{ij},$$

$$a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}),$$

$$b_{ij} = \frac{b_i + b_j}{2},$$

where x_i is the mole fraction of the i^{th} component, k_{ij} is a concentration independent interaction parameter between components i and j . The interaction parameters can be assumed to be constants or can be adjusted to fit experimentally obtained thermodynamic equilibrium data by assuming them to be functions of component critical temperatures via

$$1 - k_{ij} = \left[\frac{2\sqrt{T_{ci}T_{cj}}}{T_{ci} + T_{cj}} \right]^n.$$

GAMMA DISTRIBUTION FUNCTION

It has been reported in literature that gamma distribution function is a suitable candidate to represent molecular weight of associated asphaltene molecules in phase

behavior calculations (Huang and Radosz 1991; Alboudwarej et al. 2003). The asphaltene fraction represented with a Gamma distribution for molecular weight is given by

$$f(MW) = \frac{(MW - MW_m)^{\beta-1}}{\Gamma(\beta)} \left[\frac{\beta}{MW_{Avg} - MW_m} \right]^\beta \times \exp \left(\beta \frac{MW - MW_m}{MW_{Avg} - MW_m} \right),$$

where MW is the molecular weight, MW_{Avg} is the average weight of asphaltene aggregates, MW_m is the weight of a single monomer in the asphaltene aggregate, β is a shape factor and $\Gamma(\beta)$ is the gamma distribution function with the shape factor as the parameter. Díaz et al. (2011) reported using $\beta = 2.5$, $MW_m = 760 \text{ g/mol}$ and $MW_m = 1800 \text{ g/mol}$ while applying the gamma distribution function to describe asphaltene molecular weight using the CEoS model.

CUBIC PLUS ASSOCIATION (CPA) EoS

As per CPA framework, the excess Helmholtz free energy consists of two parts: the physical part describes the non-associating molecular interactions while the association part describes the self-association and cross-association interactions of asphaltene and aromatic/resins components. The physical contribution is represented by using PR EoS parameters and is as specified via

$$\frac{A_{ph}^{ex}}{nRT} = -\ln(1 - b\rho_c) - \frac{a}{2\sqrt{2}bRT} \ln \left(\frac{1+(1+\sqrt{2})b\rho_c}{1+(1-\sqrt{2})b\rho_c} \right),$$

where R is the universal gas constant, T is the absolute temperature, n is the total number of moles, ρ_c is the molar density of the mixture, a and b are the attractive and repulsive parameters of PR EoS, which can be derived using van der Waals mixing rules (Kwak and Mansoori 1986) for multicomponent mixtures as discussed above.

The association term is obtained from the thermodynamic perturbation theory with the assumption that there are N_A identical association sites per asphaltene molecule and N_R identical association sites per aromatic/resin molecule.

$$\frac{A_{assoc}^{ex}}{nRT} = N_A x_A \left(\ln \chi_A + \frac{1 - \chi_A}{2} \right) + N_R x_R \left(\ln \chi_R + \frac{1 - \chi_R}{2} \right),$$

The subscripts ‘A’ and ‘R’ represent asphaltene and aromatic/resin components and χ_A and χ_R are their mole fractions not bonded at one of the association sites respectively. These can be calculated via

$$\chi_A = \frac{1}{1 + \rho_c N_A x_A \chi_A \Delta^{AA} + \rho_c N_R x_R \chi_R \Delta^{AR}},$$

$$\chi_R = \frac{1}{1 + \rho_c N_A x_A \chi_A \Delta^{AR}},$$

$$\Delta^{ij} = g \kappa_{ij} b_{ij} [\exp(\epsilon_{ij}/\kappa T) - 1] \quad (i = A, j = A \text{ or } R),$$

and

$$g \approx \frac{(1 - 0.5 \eta)}{(1 - \eta)^3} \text{ where } \eta = b \rho_c / 4,$$

where Δ^{ij} is the association strength, κ is the Boltzmann constant, g is the contact value of the radial distribution of the hard-sphere mixture, and κ_{ij} and ϵ_{ij} are the association volume and energy parameters, respectively.

PERTURBED CHAIN STATISTICAL FLUID ASSOCIATION THEORY (PC-SAFT) EoS

As discussed before, three parameters are required in PC-SAFT EoS for characterizing each non-associating component namely, number of segments per molecule (m), temperature independent diameter of each molecular segment (σ) and segment-segment dispersion (attractive) energy (ϵ). As stated by Gross and Sadowski (2001), the reduced Helmholtz energy of a fluid is the addition of the reduced Helmholtz energy of the hard chain (reference term) and the change in reduced Helmholtz energy due to displacement and association (perturbation term), which is mathematically described as

$$\tilde{a}^{res} = \tilde{a}^{hc} + \tilde{a}^{disp} + \tilde{a}^{assoc},$$

where \tilde{a} is the reduced free Helmholtz energy and is defined as

$$\tilde{a} = \frac{A}{N\kappa T},$$

$$\tilde{a}^{hc} = \bar{m} \tilde{a}^{hs} - \sum_{i=1}^{N_c} x_i (m_i - 1) \ln g_{ii}^{hs}(d_{ii}),$$

$$\bar{m} = \sum_{i=1}^{N_c} x_i m_i,$$

$$\tilde{a}^{hs} = \frac{1}{\xi_0} \left[\frac{3\xi_1\xi_2}{(1-\xi_3)} + \frac{\xi_2^3}{\xi_3(1-\xi_3)^2} + \frac{\xi_2^3}{\xi_3^2} \ln(1-\xi_3) \right],$$

$$\xi_n = \frac{\pi}{6} \rho \sum_{i=1}^{N_c} x_i m_i d_i^n \quad \text{for } n = 0, 1, 2, 3,$$

$$g_{ij}^{hs} = \frac{1}{(1-\xi_3)} + \left(\frac{d_i d_j}{d_i + d_j} \right) \frac{3\xi_2}{(1-\xi_3)^2} + \left(\frac{d_i d_j}{d_i + d_j} \right)^2 \frac{3\xi_2^3}{(1-\xi_3)^3},$$

for $i, j = 1, \dots, N_c$,

$$d_i(T) = \sigma_i [1 - 0.12 \exp(-\frac{3\varepsilon_i}{\kappa T})],$$

where, ρ is the number density, d_{ii} is the temperature-dependent segment diameter of component i and σ_i is the adjustable PC-SAFT temperature independent segment diameter. Tables 1 and 2 shows the PC-SAFT correlations for the three parameters for saturates and the aromatics + resins pseudocomponents as given by Gross and Sadowski (2001).

Table 1. PC-SAFT parameter correlations for saturates.

Parameter	Function
m	$(0.0257 \times MW) + 0.8444$
$\sigma(A)$	$4.047 - \frac{4.8013 \times \ln(MW)}{MW}$
$\varepsilon(K)$	$\exp\left(5.5769 - \frac{9.523}{MW}\right)$

Table 2. PC-SAFT parameter correlations for aromatics + resins.

PC-SAFT parameter correlations for aromatics + resins pseudo component as a function of molecular weight. The equations are of the form, Parameter = $(1 - \gamma)(\text{Benzene derivatives correlation}) + \gamma(\text{Poly-nuclear-aromatic correlation})$.

Parameter	Function
m	$(1 - \gamma)(0.0223 \times MW + 0.751) + \gamma(0.0101 \times MW + 1.7296)$
$\sigma(A)$	$(1 - \gamma)\left(4.1377 - \frac{38.1483}{MW}\right) + \gamma\left(4.6169 - \frac{93.98}{MW}\right)$
$\varepsilon(K)$	$(1 - \gamma)(0.00436 \times MW + 283.93) + \gamma\left(508 - \frac{234100}{(MW)^{1.5}}\right)$

Nomenclature

δ = Hildebrand Solubility Parameter

CED = Cohesive Energy Density

ΔH = Heat of Vaporization

n = Number of moles

P = Pressure

R = Gas Constant

T = Temperature

MW = Molecular weight

V_m = Molar Liquid Volume

P_c = Critical Pressure

T_c = Critical Temperature

ω = Acentric Factor

x = Mole fraction

A = Helmholtz Energy

A^{segment} = Helmholtz Energy of the free segment

ΔA^{chain} = Change in Helmholtz Energy due to chain formation

ΔA^{assoc} = Change in Helmholtz Energy due to association

A^{hc} = Helmholtz Energy of hard chains

A^{hs} = Helmholtz Energy of hard spheres

A^{ex} = Excess Helmholtz Energy

\tilde{a} = Reduced Helmholtz energy

m = Number of segments per molecule (PC-SAFT)

σ = Temperature independent diameter of each molecular segment (PC-SAFT)

ε = Segment-segment dispersion (attractive) energy (PC-SAFT)

N = Avogadro's Number (6.022×10^{23})

κ = Boltzmann Constant ($1.38 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$)

k = Binary Interaction Parameter (BIP)

a = Attractive term (PR EoS)

b = Repulsive term (PR EoS)

Γ = Gamma distribution function

α = Tuning parameter for PR EoS, function of acentric factor and T

β = Shape factor

ρ_c = Molar density of the mixture

χ = Mole fraction of the component that is not bonded at an association site

ρ = Number density (PC-SAFT)

References

- Alboudwarej, Hussein et al. 2003. "Regular Solution Model for Asphaltene Precipitation from Bitumens and Solvents." *AIChE Journal* 49(11): 2948–56.
- Andersen, Simon I, and James G Speight. 1999. "Thermodynamic Models for Asphaltene Solubility and Precipitation." *Journal of Petroleum Science and Engineering* 22(1–3): 53–66. https://ac.els-cdn.com/S0920410598000576/1-s2.0-S0920410598000576-main.pdf?_tid=9c0018da-11cf-11e8-be6c-00000aabb0f02&acdnat=1518644581_4501dea80b51ccb728637af224165128 (February 14, 2018).
- Arciniegas, Laura Moreno, and Tayfun Babadagli. 2014. "Asphaltene Precipitation, Flocculation and Deposition during Solvent Injection at Elevated Temperatures for Heavy Oil Recovery." *Fuel* 124: 202–11. https://ac.els-cdn.com/S001623611400129X/1-s2.0-S001623611400129X-main.pdf?_tid=e67559f5-6e02-4a3f-8ccf-7167937290a0&acdnat=1523290636_58a8154147112f3e5f6f5cba03b86e0f (April 9, 2018).
- Arya, Alay, Xiaodong Liang, Nicolas Von Solms, and Georgios M Kontogeorgis. 2016. "Modeling of Asphaltene Onset Precipitation Conditions with Cubic Plus Association (CPA) and Perturbed Chain Statistical Associating Fluid Theory (PC-SAFT) Equations of State." *Energy and Fuels* 30(8): 6835–52. <https://pubs.acs.org/doi/pdf/10.1021/acs.energyfuels.6b00674> (March 28, 2018).
- Ashoori, S, A. Abedini, R Abedini, and Kh Qorbani Nasheghi. 2010. "Comparison of Scaling Equation with Neural Network Model for Prediction of Asphaltene Precipitation." *Journal of Petroleum Science and Engineering* 72(1–2): 186–94. https://ac.els-cdn.com/S0920410510000616/1-s2.0-S0920410510000616-main.pdf?_tid=97f3eef6-a592-4f7d-b5a2-38a52fcbdf97&acdnat=1525203686_e660fd8ab182f40e47267e164fecfc7e (May 1, 2018).
- Bagheri, M B et al. 2009. "Developing a New Scaling Equation for Modelling of Asphaltene Precipitation." : 16–18. <https://www.onepetro.org/download/conference-paper/PETSOC-2009-039?id=conference-paper%2FPETSOC-2009-039> (May 1, 2018).
- De Boer, R B, Klaas Leerlooyer, M R P Eigner, and A R D Van Bergen. 1995. "Screening of Crude Oils for Asphalt Precipitation: Theory, Practice, and the Selection of Inhibitors." *SPE Production & Facilities* 10(01): 55–61.
- Burke, John. 1984. "Solubility Parameters: Theory and Application." <https://cool.conservation-us.org/coolaic/sg/bpg/annual/v03/bp03-04.html>.
- Chung, Ting-horng. 1992. "Thermodynamic Modeling for Organic Solid Precipitation." *SPE Journal*.

- Cimino, Roberto, Sebastian Corraera, P a Sacomani, and Carlo Camiani. 1995. "Thermodynamic Modelling for Prediction of Asphaltene Deposition." *Society of Petroleum Engineers Journal* 28993: 14. <https://www.onepetro.org/download/conference-paper/SPE-28993-MS?id=conference-paper%2FSPE-28993-MS> (February 14, 2018).
- David Ting, P., George J. Hirasaki, and Walter G. Chapman. 2003. "Modeling of Asphaltene Phase Behavior with the SAFT Equation of State." *Petroleum Science and Technology* 21(3-4): 647-61. <http://www.tandfonline.com/doi/abs/10.1081/LFT-120018544>.
- Díaz, O. Castellanos, J Modaresghazani, M.A. Satyro, and H.W. Yarranton. 2011. "Modeling the Phase Behavior of Heavy Oil and Solvent Mixtures." *Fluid Phase Equilibria* 304(1): 74-85. http://ac.els-cdn.com/S037838121100094X/1-s2.0-S037838121100094X-main.pdf?_tid=ce620e2c-26e9-11e7-8903-00000aab0f01&acdnat=1492817309_52a336b69310770b33f4566b3bc5599c (April 21, 2017).
- Escobedo, Joel, and G A Mansoori. 1997. "Viscometric Principles of Onsets of Colloidal Asphaltene Flocculation in Paraffinic Oils and Asphaltene Micellization in Aromatics." *SPE Production & Facilities* 12(02): 116-22.
- Flory, Paul J. 1942. "Thermodynamics of High Polymer Solutions." *The Journal of Chemical Physics*.
- Gao, Jianyi, and Huazhou Andy Li. 2017. "A Phase-Behavior Study for n-Hexane/Bitumen and n-Octane/Bitumen Mixtures." *SPE* 186097. <https://www.onepetro.org/download/journal-paper/SPE-186097-PA?id=journal-paper%2FSPE-186097-PA> (July 26, 2017).
- Gao, Jianyi, Ryosuke Okuno, and Huazhou Andy Li. 2016. "An Experimental Study of Multiphase Behavior for N-Butane/Bitumen/Water Mixtures." In *SPE Canada Heavy Oil Technical Conference*, 1-32. <https://www.onepetro.org/download/journal-paper/SPE-180736-PA?id=journal-paper%2FSPE-180736-PA> (July 26, 2017).
- Gonzalez, Doris L, P David Ting, George J Hirasaki, and Walter G Chapman. 2005. "Prediction of Asphaltene Instability under Gas Injection with the PC-SAFT Equation of State." *Energy and Fuels* 19(4): 1230-34. http://porousmedia.rice.edu/resources/EnergyFuels_2005_Gas_Injection.pdf (May 1, 2017).
- Gross, Joachim, and Gabriele Sadowski. 2001. "Perturbed-Chain SAFT: An Equation of State Based on a Perturbation Theory for Chain Molecules." *Industrial & Engineering Chemistry Research* 40(4): 1244-60. <http://dns2.asia.edu.tw/~ysho/YSHO-English/1000 CE/PDF/Ind Eng Che Res40, 1244.pdf> (May 1, 2017).

- Hirschberg, Ade, L N J DeJong, B A Schipper, and J G Meijer. 1984. "Influence of Temperature and Pressure on Asphaltene Flocculation." *Society of Petroleum Engineers Journal* 24(03): 283–93.
- Hu, Y. F., G. J. Chen, J. T. Yang, and T. M. Guo. 2000. "A Study on the Application of Scaling Equation for Asphaltene Precipitation." *Fluid Phase Equilibria* 171(1–2): 181–95. www.elsevier.nl/locate/fluid (May 1, 2018).
- Huang, S H, and M Radosz. 1991. "Phase Behavior of Reservoir Fluids III: Molecular Lumping and Characterization." *Fluid phase equilibria* 66(1–2): 1–21.
- Khoshandam, Ali, and Abdolmohammad Alamdari. 2010. "Kinetics of Asphaltene Precipitation in a Heptane–Toluene Mixture." *Energy & Fuels* 24(3): 1917–24. <https://doi.org/10.1021/ef9012328>.
- Koots, J. Anne, and James G. Speight. 1975. "Relation of Petroleum Resins to Asphaltenes." *Fuel*.
- Kwak, T Y, and G A Mansoori. 1986. "Van Der Waals Mixing Rules for Cubic Equations of State. Applications for Supercritical Fluid Extraction Modelling." *Chemical engineering science* 41(5): 1303–9.
- Lee, Byung Ik, and Michael G Kesler. 1975. "A Generalized Thermodynamic Correlation Based on Three-parameter Corresponding States." *AIChE Journal* 21(3): 510–27.
- Leekumjorn, Sukit, and Kristian Krejbjerg. 2013. "Phase Behavior of Reservoir Fluids: Comparisons of PC-SAFT and Cubic EOS Simulations." *Fluid Phase Equilibria* 359: 17–23. http://ac.els-cdn.com/S0378381213003464/1-s2.0-S0378381213003464-main.pdf?_tid=44ae30-8f48-11e7-b283-00000aacb35f&acdnat=1504292801_9bbae9c935ba2daf3c03af09b0e2b849 (September 1, 2017).
- Leontaritis, K J, and G A Mansoori. 1987. "SPE 16258 Asphaltene Flocculation During Oil Production A Thermodynamic Colloidal Model." *Society of Petroleum Engineers*. https://www.researchgate.net/profile/G_Ali_Mansoori/publication/254521040_Aspphaltene_Flocculation_During_Oil_Production_and_Processing_A_Thermodynamic_Colloidal_Model/links/00b4953b1f58b7807e000000.pdf (November 28, 2018).
- Li, Zhidong, and Abbas Firoozabadi. 2010. "Modeling Asphaltene Precipitation by N-Alkanes from Heavy Oils and Bitumens Using Cubic-plus-Association Equation of State." *Energy and Fuels* 24(2): 1106–13. <http://pubs.acs.org/doi/pdf/10.1021/ef9009857> (June 1, 2017).
- Mitchell, D L, and J G Speight. 1973. "Solubility of (Athabasca Bitumen) Asphaltenes in (44) Hydrocarbon Solvents."
- Mullins, Oliver C et al. 2012. "Advances in Asphaltene Science and the Yen-Mullins Model." In *Energy and Fuels*, , 3986–4003. <https://pubs.acs.org/doi/pdf/10.1021/ef300185p> (February 14, 2018).

- Nghiem, L X, M S Hassam, Ram Nutakki, and A E D George. 1993. "Efficient Modelling of Asphaltene Precipitation." *Proceedings - SPE Annual Technical Conference and Exhibition* Sigma: 375–84. <https://www.onepetro.org/download/conference-paper/SPE-26642-MS?id=conference-paper%2FSPE-26642-MS> (February 14, 2018).
- Nor-Azlan, N, and M A Adewumi. 1993. "Development of Asphaltene Phase Equilibria Predictive Model." In *SPE Eastern Regional Meeting*,.
- Oilfield Wiki. 2016. "Asphaltenes." <http://www.oilfieldwiki.com/wiki/Asphaltenes>.
- Oliver Mullins, R C, Bruno Martínez-Haya, and Alan G Marshall. 2008. "Contrasting Perspective on Asphaltene Molecular Weight. This Comment vs the Overview of A." *Energy & Fuels* (22): 1765–73. <https://pubs-acsc-org.ezproxy.lib.utexas.edu/doi/pdf/10.1021/ef700714z> (March 29, 2018).
- Östlund, J-A, J-E Löfroth, K Holmberg, and M Nyden. 2002. "Flocculation Behavior of Asphaltenes in Solvent/Nonsolvent Systems." *Journal of colloid and interface science* 253(1): 150–58.
- Östlund, Jenny-Ann, Sven-Ingvar Andersson, and Magnus Nydén. 2001. "Studies of Asphaltenes by the Use of Pulsed-Field Gradient Spin Echo NMR." *Fuel* 80(11): 1529–33.
- Pan, Huanquan, and Abbas Firoozabadi. 2000. "Thermodynamic Micellization Model for Asphaltene Precipitation From Reservoir Crudes at High Pressures and Temperatures." *SPE Production & Facilities* 15(August 1999): 5–8. <https://www.onepetro.org/download/conference-paper/SPE-38857-MS?id=conference-paper%2FSPE-38857-MS> (February 15, 2018).
- Panuganti, Sai R. et al. 2013. "SAFT Model for Upstream Asphaltene Applications." *Fluid Phase Equilibria* 359: 2–16.
- Panuganti, Sai R et al. 2012. "PC-SAFT Characterization of Crude Oils and Modeling of Asphaltene Phase Behavior." *Fuel* 93: 658–69. http://ac.els-cdn.com/S0016236111005886/1-s2.0-S0016236111005886-main.pdf?_tid=b02e4f50-2e92-11e7-8d2a-00000aacb35f&acdnat=1493659501_caa2eba33b8a26aae1f8966ae75da01b (May 1, 2017).
- Priyanto, Slamet, G Ali Mansoori, and Aryadi Suwono. 2001. "Measurement of Property Relationships of Nano-Structure Micelles and Coacervates of Asphaltene in a Pure Solvent." *Chemical Engineering Science* 56(24): 6933–39.
- Qin, Xiangjun, Peng Wang, Kamy Sepehrnoori, and Gary A Pope. 2000. "Modeling Asphaltene Precipitation in Reservoir Simulation." *Industrial & Engineering Chemistry Research* 39(8): 2644–54. <http://pubs.acs.org/doi/pdf/10.1021/ie990781g> (December 4, 2017).

- Rassamdana, Hossein et al. 1996. "Asphalt Flocculation and Deposition: I. The Onset of Precipitation." *AIChE Journal* 42(1): 10–22. <https://onlinelibrary.wiley.com/doi/pdf/10.1002/aic.690420104> (May 1, 2018).
- Robinson, Donald B, and Ding-Yu Peng. 1978. *The Characterization of the Heptanes and Heavier Fractions for the GPA Peng-Robinson Programs*. Gas processors association.
- Rogel, E, and L Carbognani. 2003. "Density Estimation of Asphaltenes Using Molecular Dynamics Simulations." <https://pubs.acs.org/sharingguidelines> (November 26, 2018).
- Saajanlehto, Meri, and Ville Alopaeus. 2014. "Heavy Oil Characterization Method for PC-SAFT." *Fuel* 133: 216–23. http://ac.els-cdn.com/S0016236114004670/1-s2.0-S0016236114004670-main.pdf?_tid=8b298d90-8f4b-11e7-94f9-00000aab0f01&acdnat=1504294208_c96727457e64a353b84eda498966b980 (September 1, 2017).
- Sabbagh, O et al. 2006. "Applying the PR-EoS to Asphaltene Precipitation from n-Alkane Diluted Heavy Oils and Bitumens." *Energy and Fuels* 20(2): 625–34. <http://pubs.acs.org/doi/pdf/10.1021/ef0502709> (May 17, 2017).
- Sayyad Amin, J., S. Alimohammadi, and S. Zendeboudi. 2017. "Systematic Investigation of Asphaltene Precipitation by Experimental and Reliable Deterministic Tools." *Canadian Journal of Chemical Engineering* 95(7): 1388–98.
- Sayyad Amin, Javad et al. 2010. "Prediction of Asphaltene Precipitation: Learning from Data at Different Conditions." *Energy & Fuels* 24(7): 4046–53. <https://pubs.acs.org/doi/pdf/10.1021/ef100106r> (May 1, 2018).
- Sheu, Oliver C. Mullins and Eric Y. 2013. Springer Science *Structures and Dynamics of Asphaltenes*.
- Sirota, Eric B, and Min Y Lin. 2007. "Physical Behavior of Asphaltenes." *Energy & Fuels* 21(5): 2809–15. <https://doi.org/10.1021/ef060634c>.
- Speight, J G. 2004. "Petroleum Asphaltenes - Part 1: Asphaltenes, Resins and the Structure of Petroleum." *Oil and Gas Science and Technology* 59(5): 467–77. https://ogst.ifpenergiesnouvelles.fr/articles/ogst/pdf/2004/05/speight1_vol59n5.pdf (April 9, 2018).
- Speight, James G., Robert B. Long, and Theodore D. Trowbridge. 1984. "Factors Influencing the Separation of Asphaltenes from Heavy Petroleum Feedstocks." *Fuel*.
- Ting, Pd, and Dl Gonzalez. 2007. "Application of the PC-SAFT Equation of State to Asphaltene Phase Behavior." *Asphaltenes, Heavy Oils, ...*: 1–4. http://link.springer.com/chapter/10.1007/0-387-68903-6_12.

- Twu, Chornng H. 1984. "An Internally Consistent Correlation for Predicting the Critical Properties and Molecular Weights of Petroleum and Coal-Tar Liquids." *Fluid phase equilibria* 16(2): 137–50.
- Vargas, Francisco M., Jeff L. Creek, and Walter G. Chapman. 2010. "On the Development of an Asphaltene Deposition Simulator." *Energy and Fuels* 24(4): 2294–99. <http://pubs.acs.org/doi/pdf/10.1021/ef900951n> (July 25, 2017).
- Vargas, Francisco M., Doris L. Gonzalez, George J. Hirasaki, and Walter G. Chapman. 2009. "Modeling Asphaltene Phase Behavior in Crude Oil Systems Using the Perturbed Chain Form of the Statistical Associating Fluid Theory (PC-SAFT) Equation of State." *Energy and Fuels* 23(3): 1140–46. <http://pubs.acs.org/doi/pdf/10.1021/ef8006678> (July 25, 2017).
- Vargas, Francisco M, Doris L Gonzalez, Jefferson L Creek, et al. 2009. "Development of a General Method for Modeling Asphaltene Stability †." *Energy & Fuels* 23(3): 1147–54. <https://pubs.acs.org/doi/pdf/10.1021/ef800666j> (February 14, 2018).
- Wang, J X, and J S Buckley. 2001. "A Two-Component Solubility Model of the Onset of Asphaltene Flocculation in Crude Oils." *Energy and Fuels* 15(5): 1004–12. <https://pubs.acs.org/doi/pdf/10.1021/ef010012l> (February 14, 2018).
- Yarranton, Harvey W., and Jacob H. Masliyah. 1996. "Molar Mass Distribution and Solubility Modeling of Asphaltenes." *AIChE Journal* 42(12): 3533–43. <http://doi.wiley.com/10.1002/aic.690421222>.
- Zahedi, G et al. 2009. "Prediction of Asphaltene Precipitation in Crude Oil." *Journal of Petroleum Science and Engineering* 68(3–4): 218–22.
- Zendehboudi, Sohrab et al. 2014. "Asphaltene Precipitation and Deposition in Oil Reservoirs - Technical Aspects, Experimental and Hybrid Neural Network Predictive Tools." *Chemical Engineering Research and Design* 92(5): 857–75. http://www.mun.ca/engineering/research/eor/publications/Zendehboudi,_S._et_al,_2014.pdf (May 1, 2018).
- Zúñiga-Hinojosa, María A. et al. 2014. "Modeling of Asphaltene Precipitation from N-Alkane Diluted Heavy Oils and Bitumens Using the PC-SAFT Equation of State." *Fluid Phase Equilibria* 376: 210–24. http://ac.els-cdn.com/S0378381214003379/1-s2.0-S0378381214003379-main.pdf?_tid=4f8f9dd8-724a-11e7-b6cc-00000aacb361&acdnat=1501105095_ced5d311f5ef2e3ead8ba5389873e5c4 (July 26, 2017).